

Comparisons of polarization switching in “hard,” “soft,” and relaxor ferroelectrics

Christelle Jullian, J. F. Li, and D. Viehland

Citation: *Journal of Applied Physics* **95**, 4316 (2004); doi: 10.1063/1.1641962

View online: <http://dx.doi.org/10.1063/1.1641962>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/95/8?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Electric-field-controlled interface strain coupling and non-volatile resistance switching of La_{1-x}BaxMnO₃ thin films epitaxially grown on relaxor-based ferroelectric single crystals](#)

J. Appl. Phys. **116**, 113911 (2014); 10.1063/1.4896172

[Mapping bias-induced phase stability and random fields in relaxor ferroelectrics](#)

Appl. Phys. Lett. **95**, 092904 (2009); 10.1063/1.3222868

[Broadband inelastic light scattering of a relaxor ferroelectric 0.71 Pb \(Ni 1/3 Nb 2/3 \) O 3 - 0.29 Pb Ti O 3](#)

Appl. Phys. Lett. **89**, 212903 (2006); 10.1063/1.2393159

[Ferroelectric behavior in nominally relaxor lead lanthanum zirconate titanate thin films prepared by chemical solution deposition on copper foil](#)

Appl. Phys. Lett. **88**, 262907 (2006); 10.1063/1.2217254

[Direct piezoelectric effect in relaxor-ferroelectric single crystals](#)

J. Appl. Phys. **95**, 5679 (2004); 10.1063/1.1703829



MIT LINCOLN LABORATORY CAREERS

Discover the satisfaction of innovation and service to the nation

- Space Control
- Air & Missile Defense
- Communications Systems & Cyber Security
- Intelligence, Surveillance and Reconnaissance Systems
- Advanced Electronics
- Tactical Systems
- Homeland Protection
- Air Traffic Control

LINCOLN LABORATORY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY



[LEARN MORE](#)

Comparisons of polarization switching in “hard,” “soft,” and relaxor ferroelectrics

Christelle Jullian, J. F. Li, and D. Viehland^{a)}

Department of Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia 24061

(Received 20 August 2003; accepted 17 November 2003)

The dynamics of polarization switching have been investigated over extremely broad time ($10^{-8} < t < 10^2$ s) and field ranges for hard, soft, and relaxor ferroelectrics based on aliovalent modified $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$. The results unambiguously demonstrate important differences in the polarization switching mechanism for these various types of ferroelectrics. © 2004 American Institute of Physics. [DOI: 10.1063/1.1641962]

I. INTRODUCTION

Defects and substituents are known to significantly influence the electromechanical properties of ferroelectrics.^{1,2} Various classifications of piezoelectric behaviors have been categorized in lead zirconate titanate (PZT). The basic two types of classifications are commonly called “soft” and “hard.”² In general, higher valent substituents induce soft piezoelectric behavior, where as lower valent ones induce hard. With increasing higher valent substituent concentration, a cross over between soft and relaxor ferroelectric behavior occurs.

Soft ferroelectrics have lower coercive fields, higher hysteretic losses, higher dielectric and mechanical loss factors, and lower remanent polarizations and strains, relative to hard ones.^{1,2} The extra contribution is designated as extrinsic, and is believed to be due to domain dynamics under weak ac fields. Hard ferroelectrics have an asymmetric polarization versus electric field (P - E) response, which is shifted by a built-in potential.³ The built-in potential is due to a pinning of the polarization by dipolar defects. Relaxor ferroelectrics have a frequency dispersive dielectric response in the audio range;^{4,5} the inability to sustain remanence for temperatures above a freezing temperature T_f , which is notably less than that of the dielectric maximum (T_m);⁶ and by the presence of a local polarization until $T \gg T_m$.⁷

Previous transmission electron microscopy (TEM) studies of soft, hard, and relaxor ferroelectrics have shown dramatic differences in domain stability.⁸⁻¹² Studies of hard ferroelectrics have shown fine “wavy” domains.^{8,9} Comparisons with dielectric property data indicated that the wavy domains result from pinning effects. Systematic studies of soft ferroelectrics have shown the development of increasingly irregular domain morphologies with increasing higher valent substituent concentrations.^{10,11} And, above a critical concentration, polar nanodomains (PNR) form that have an average diameter between 30 and 50 Å,^{11,12} which is the relaxor state.^{4,5}

Domain dynamics are generally believed to make significant contributions to ferroelectric and piezoelectric properties. However, understanding them has proven difficult, in

particular in systems containing significant concentrations of aliovalent substituents. Limiting the study of polarization switching and domain dynamics has been that current transient investigations have been performed over relatively narrow time (t) and electric field (E) ranges¹³⁻²⁰—even though the current response is known to be logarithmic in time.^{16,21-23} Nucleation and growth (N&G) models have previously been developed. However, analysis of the dynamics in the time domain of $10^{-8} < t < 10^{-6}$ s provides incomplete information, upon which to develop a comprehensive mechanistic understanding. Previous N&G models¹³⁻²⁰ have been based on nucleation sites confined to existing domain walls [i.e., two dimensional (2D)] with a subsequent restriction that during growth, the domain walls remain coherent (i.e., one-dimensional). However, it is doubtful that such a model can explain switching in a wider range of aliovalently modified ferroelectrics.

Investigations of the polarization dynamics over broad time and field regions would be greatly important to the study of modified ferroelectrics. In this article, we report the polarization dynamics over such a broad time domain (extending from $10^{-8} < t < 10^2$ s) for hard, soft, and relaxor ferroelectrics based on PZT. The results unambiguously demonstrate important differences in switching mechanisms between these general types of ferroelectrics.

II. EXPERIMENTAL PROCEDURE

Polycrystalline specimens of soft PZT ($E_c \sim 11$ kV/cm) and hard PZT specimens were obtained from EDO Corp. (Salt Lake City, UT). In addition, PLZT 10/65/35 relaxor specimens were prepared, as previously reported.^{10,11} The specimens were cut into typical dimensions of 0.3 mm in thickness and 4 mm² in area, and were electroded with gold. Measurements were performed for various fields. In order to measure the response of the specimens over a broad time domain from $10^{-8} < t < 10^2$ s, three different measurements circuits were developed and built, as recently reported.²⁴ To prepare for switching, both sides of the specimen were raised to the desired switching field. Then, at time $t = 0$, one side of the specimen was taken to ground. By using these steps, we can certify that high voltage reaches its full maximum, before the polarization starts to rise. It was found that switching

^{a)}Electronic mail: dviehland@vt.edu

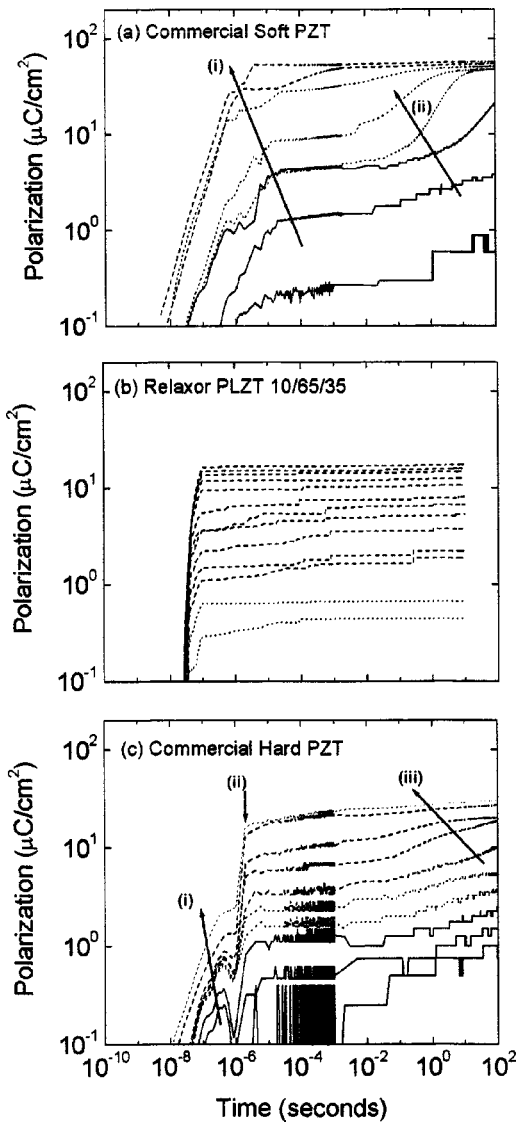


FIG. 1. Logarithm of polarization as a function of logarithm of time for various modified PZT ferroelectrics over broad time and field ranges: (a) soft PZT [from bottom to top, $E=2, 6, 8, 9, 10, 12, 16,$ and 23 kV/cm], (b) relaxor PLZT 10/65/35 [from bottom to top, $E=1.25, 1.75, 2.75, 4, 6, 8, 10, 12, 16, 19, 21, 23,$ and 25 kV/cm], and (c) hard PZT [from bottom to top, $E=5, 10, 13, 16, 18, 19, 22, 26, 29,$ and 31 kV/cm]. Data are shown for various fields in each figure.

times of $\ll 10^{-8}$ s could be achieved. An Agilent oscilloscope operated in a time capture mode was used to measure the output voltage from each circuit.

III. RESULTS AND DISCUSSION

Figure 1 shows the logarithm of the polarization as a function of the logarithm of time for [Fig. 1(a)] a soft PZT, [Fig. 1(b)] a relaxor PLZT 10/65/35, and [Fig. 1(c)] a hard PZT. These data were all taken at room temperature. Data are shown for over ten decades in time, taken at various applied electric fields. The data can be seen to be quite different for the three types of ferroelectrics.

The response of soft PZT can clearly be seen to be extremely broad in the time domain, extending over decade(s) of orders in magnitude. Two evolutionary stages in the time

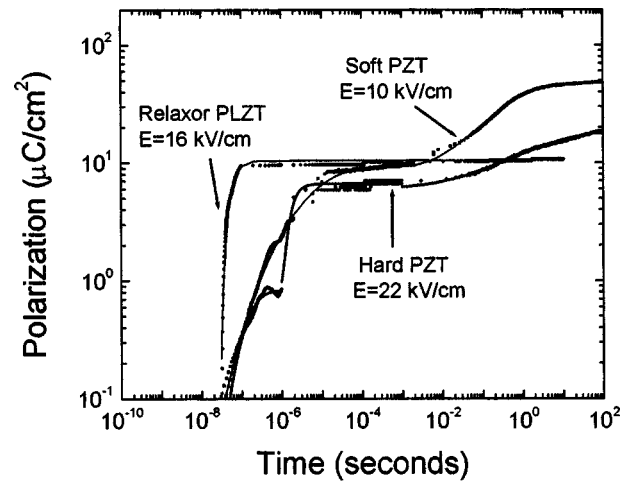


FIG. 2. Illustration of fitting of time domain polarization response for soft, hard, and relaxor ferroelectrics.

domain were found during polarization switching with increasing E . Figure 1(a) demonstrates a broad polarization transient in the time domain of $10^{-6} < t < 10^{-4}$ s designated by the symbol (i) in the figure, followed by a delay, and a subsequent second broad polarization transient in the long-time domain designated by (ii). These two stages in the time domain response represent nucleation events and domain growth events, respectively. Recent investigations²⁴ of poled $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\% \text{PbTiO}_3$ crystals have similarly shown two broad transients, demonstrating that the broadness in the time domain is not due to a variety of extrinsic pinning sites, such as grain boundaries and dislocations. With increasing E , both transients in Fig. 1(a) shifted to shorter times, but only becoming sharp at high fields of $E \gg E_c$ and short times of $t < 10^{-6}$ s.

The time dependence of the polarization for soft PZT did not follow the Avrami (AV) equation, i.e., $P(t) = P_0 \exp[-(t/\tau)^n]$, where τ is the relaxation time and n is a dimensionality constant. Rather, as shown in Fig. 2 (red line), it fit to a stretched exponential (SE) function, where terms in (t/τ) in the AV equation are replaced by ones in $\ln(t/\tau)$, i.e., $P(t) = P_0 \exp[-a(\ln(t/\tau))^n]$. This demonstrates that the N&G events are extremely broadened in the time domain. Analysis with the SE equation yielded a value of $n=3$ for nucleation, and $n=2$ for growth. Nucleation is a three-dimensional process, and not confined to domain walls. Domain growth is a 2D process, where the walls are not restricted to remain coherent. These results show that the domains walls are extremely diffuse during switching in soft PZT, and is consistent with prior TEM studies that have shown irregular domain morphologies.

The relaxor PLZT 10/65/35 can be seen to have a very sharp response near $t = 5 \times 10^{-8}$ s, as shown in Fig. 1(b). This sharp response did not shift in the time domain with increasing E , although the magnitude of the induced polarization did increase. The polarization only slightly increased with time for $t > 10^{-7}$ s. No secondary transient was found at longer times. It is relevant to note that at room temperature, PLZT 10/65/35 has slim loop $P-E$ behavior and that $T > T_f$ (see Fig. 3). The time dependence of the polarization

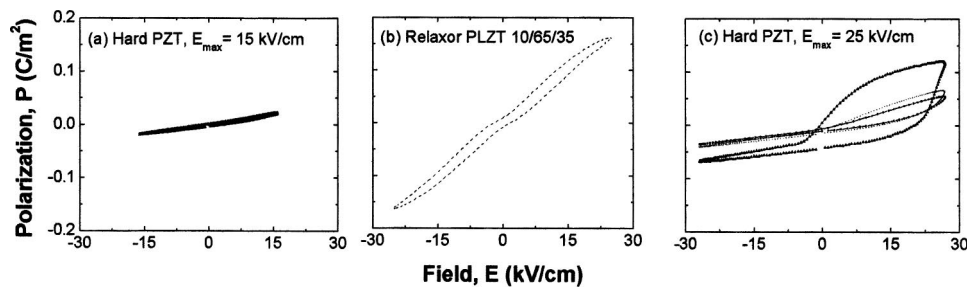


FIG. 3. P - E response for (a) hard PZT with $E = 15$ kV/cm, (b) relaxor PLZT 10/65/35 with $E = 25$ kV/cm, and (c) hard PZT with $E = 25$ kV/cm. Please notice the an hysteretic nature of (a) and (b), whereas (c) exhibits dramatically increased hysteresis with decreasing measurement frequency.

for relaxor PLZT was found to be well fit to the AV equation, as shown in Fig. 2 (blue line). Analysis yielded $n=3$ and $\tau = 4.8 \times 10^{-8}$ s. No indication of a domain growth region was found. These results demonstrate that polarization reversal in the relaxors for $T > T_f$ occurs entirely by nucleation. The results are consistent with prior TEM studies that have shown pre-existing polar nuclei or PNR^{11,12} under zero field.

Hard PZT was found to have three evolutionary stages. Figure 1(c) shows a broad polarization transient in the time domain of $10^{-8} < t < 10^{-6}$ s designated as (i) in the figure. This transient was similar to that observed in soft PZT. Analysis with the SE equation yielded a value of $n=3$, as shown in green in Fig. 2. Then, at $t \approx 10^{-6}$ s, a sharp increase in P was found, which is designated as (ii). The sharpness of this peak is similar to that observed for the relaxor, but $\tau = 10^{-6}$ s, rather than 10^{-8} s. This portion of the time domain response was found to be well fit by the AV equation with $n=3$, and its position in the time domain did not shift with increasing E . Finally, a weak long-time polarization transient for $t > 1$ s was found at higher E , designated by (iii). It is analogous to that in soft PZT, but was much weaker and was only noticeable at much higher E . This long-time transient was well fit by the SE equation with $n=2$, again in analogy with soft PZT.

The results for hard PZT demonstrate that the switched polarization is mainly due to nucleation. The data show a switchover from SE type nucleation events to AV ones. It is important to note that the fraction of polarization switched by nucleation is much higher for hard PZT, than soft. This is because domain growth is not significant for hard PZT. The switchover to AV-type nucleation near $t = 10^{-6}$ s may reflect a transition to a state with a high density of stable polar nuclei or PNR, somewhat similar to the relaxor, which then do not grow readily into fully formed domain variants with a reversed polarization due to built-in dipolar fields.

We also found that nucleation is only slightly dissipative, whereas domain growth is strongly so. This is illustrated in the P - E curves given in Figs. 3(a)-3(c), respectively, for hard PZT with $E = 15$ kV/cm, relaxor PLZT, and hard PZT with $E = 25$ kV/cm. The P - E response for both Figs. 3(a) and 3(b) were nearly an hysteretic and nondispersive over the frequency range of $10^{-2} < f < 10^2$ Hz. Clearly, nucleation is not significantly dissipative. However, for hard PZT with $E = 25$ kV/cm, hysteresis became evident with decreasing f , as shown in Fig. 3(c). The onset of hysteresis corresponds to the

development of a long-time polarization transient in the time domain data with increasing E . These results indicate that nucleation events occur against a small anisotropy barrier. In this regard, nucleation events may be similar to polarization rotation in poled PMN-PT crystals, with gradual structural evolution. However, in our case, rotation clearly must be an inhomogeneous process.

IV. CONCLUSIONS

In summary, the polarization response of hard, soft, and relaxor ferroelectrics have been investigated over broad time and field ranges. The results unambiguously demonstrate important differences in the polarization switching mechanism between these family of materials.

ACKNOWLEDGMENTS

This research was supported by the Office of Naval Research under Grant Nos. N000140210340, N000140210126, and MURI N000140110761.

- ¹D. Berlincourt, D. Curran, and H. Jaffe, in *Physical Acoustics* edited by W. Cady (Academic New York 1964), Vol. 1.
- ²Q. Tan, J. F. Li, and D. Viehland, *Philos. Mag. B* **76**, 59 (1997).
- ³A. P. Levanyuk and A. S. Sigov, *Defects and Structural Phase Transitions* (Gordon and Breach Science, New York, 1988).
- ⁴G. Smolenskii and A. Agranovskaya, *Sov. Phys. Solid State* **1**, 1429 (1960).
- ⁵L. E. Cross, *Ferroelectrics* **76**, 249 (1987).
- ⁶D. Viehland, M. Wuttig, and L. E. Cross, *Ferroelectrics* **120**, 71 (1991).
- ⁷G. Burns and F. Dacol, *Phys. Rev. B* **28**, 2527 (1983).
- ⁸Q. Tan, Z. Xu, J.-F. Li, and D. Viehland, *J. Appl. Phys.* **80**, 5866 (1996).
- ⁹Q. Tan, J. F. Li, and D. Viehland, *Philos. Mag. B* **76**, 59 (1997).
- ¹⁰J.-F. Li, X. H. Dai, A. Chow, and D. Viehland, *J. Mater. Res.* **10**, 926 (1995).
- ¹¹X. H. Dai, Z. Xu, and D. Viehland, *Philos. Mag. B* **70**, 33 (1994).
- ¹²C. Randall, D. Barber, and R. Whatmore, *J. Microsc.* **45**, 275 (1987).
- ¹³W. J. Merz, *Phys. Rev.* **95**, 690 (1954).
- ¹⁴M. E. Drougard, *J. Appl. Phys.* **31**, 352 (1960).
- ¹⁵R. C. Miller and G. Weinreich, *Phys. Rev.* **117**, 1460 (1960).
- ¹⁶V. Shur, E. Romyantsev, and S. Makarov, *J. Appl. Phys.* **84**, 445 (1998).
- ¹⁷Y. Ishibashi and Y. Takagi, *J. Phys. Soc. Jpn.* **31**, 506 (1971).
- ¹⁸A. Levstik, M. Kosec, V. Bobnar, C. Filipic, and J. Holc, *J. Appl. Phys.*, Part 1 **36**, 2744 (1997).
- ¹⁹Y. Ishibashi, *Integr. Ferroelectr.* **2**, 41 (1992).
- ²⁰T. Song, S. Aggarwal, Y. Gallais, B. Nagaraj, R. Ramesh, and J. Evans, *Appl. Phys. Lett.* **73**, 3366 (1998).
- ²¹I. Boscolo and S. Cialdi, *J. Appl. Phys.* **91**, 6125 (2002).
- ²²D. Viehland and J. F. Li, *J. Appl. Phys.* **90**, 2995 (2001).
- ²³D. Viehland and Y. Chen, *J. Appl. Phys.* **88**, 6696 (2000).
- ²⁴C. Jullian, J. F. Li, and D. Viehland, *Appl. Phys. Lett.* **83**, 1196 (2003).